

Giant domain wall response of highly twinned ferroelastic materials

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Many ferroelastic crystals display at sufficiently low measurement frequencies a huge elastic softening below T_c which is caused by domain wall motion. Materials range from perovskites to iron based superconductors and shape memory materials. We present a model - based on Landau-Ginzburg theory including long range elastic interaction between needle shaped ferroelastic domains - to describe the observed superelastic softening. The theory predicts that the domain wall contribution to the elastic susceptibility is different for improper and proper ferroelastic materials. A test of the theory against experimental data on SrTiO_3 , KMnF_3 , LaAlO_3 , $\text{La}_{1-x}\text{Nd}_x\text{P}_5\text{O}_{14}$ and $\text{NH}_4\text{HC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ yields excellent agreement.

The macroscopic response of materials depends often on structures spanning a broad range of length and time scales. Examples of such inhomogeneous structures are precursor clusters near structural phase transitions, domains and domain walls, interfaces at first order displacive or reconstructive phase transitions, etc. They have been reported in a wide range of functional materials. Prominent cases are the enhancement of piezoelectric response [1] of nanotwinned BaTiO_3 for domain thickness below 50 nm, or the giant piezoelectric effect in ferroelectric relaxors [2] due to the high mobility of polar nanoregions [3]. Generally, domains and domain boundaries in ferroic crystals can act as structural elements for creating novel functional devices [4]. The usefulness of domain boundaries in Domain Boundary Engineering depends on the time scale of their response. Static or pinned domain boundaries can be used as functional units since they can host functional properties (ferroelectric, superconducting, etc.) which are absent in the bulk [5]. Mobile domain boundaries can lead to giant macroscopic responses, depending on the frequency of the changing external field.

In the present work we will focus on ferroelastic materials, which depending on the type of coupling between the primary order parameter η and the strains ε can be classified as proper, pseudo proper, improper or co-elastic ones [6]. Very often ferroelastic crystals consist of a large number of domains which are separated by domain boundaries [7]. Due to mechanical compatibility these domain boundaries should be planar with well defined orientation. However, in real crystals very often needle or dagger shaped domains appear [6]. There are still many open questions, e.g. concerning the stability of ferroelastic domains, their motion under an applied dynamic stress, the observed domain freezing [8] at sufficiently low temperature, etc.

Understanding the macroscopic behaviour of multidomain crystals is important for technological applications as well as for the interpretation of seismic signals of our Earth, since domain wall motion influences the low frequency elastic and anelastic behaviour of minerals at seismic frequencies (1-20 Hz). In recent years we have per-

formed quite detailed low frequency (0.1-100 Hz) measurements in a number of perovskites [8–10] with improper ferroelastic phase transitions. In all these materials we found a huge elastic softening in the low symmetric ferroelastic phase due to the influence of domain wall motion. Calculation of the domain wall response to an applied dynamic stress is hampered, since ferroelastic domains are in general metastable or even unstable objects, in contrast to ferroelectric or ferromagnetic ones, where the competition between the domain wall energy and the depolarization or demagnetization field leads to a stable domain pattern. For this reason research of ferroelastic materials has been mainly focused on first order phase front [11, 12] - or substrate [13] - stabilized arrays of ferroelastic domains. However, it was shown previously [14], that at the end of ferroelastic needle shaped domains long range elastic stress fields appear - which is reminiscent of the stray fields in ferroelectric or ferromagnetic crystals. These stress fields stabilize an array of ferroelastic domains. Very recently we have set up a Landau-Ginzburg free energy including long range elastic interactions between needle shaped domains to calculate the equilibrium domain width and the resulting macroscopic elastic response of a ferroelastic multidomain crystal [15, 16], yielding perfect agreement with the data on improper ferroelastic perovskites. In the present work we show, that this theory predicts the domain wall response to be very different for *improper* as compared to *proper* or *pseudo proper* ferroelastic phase transitions. We will demonstrate this on the examples of SrTiO_3 [15] and KMnF_3 [8] (improper), $\text{La}_{1-x}\text{Nd}_x\text{P}_5\text{O}_{14}$ (proper)[17] and $\text{NH}_4\text{HC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ (AHO, pseudo proper). AHO single crystals were grown in our lab following the procedure of Godet, et al.[18]. For the elastic measurements a dynamical mechanical analyzer (DMA7, Perkin Elmer) was used in three point bending geometry [19]. A dynamic force F_{dyn} at $f=0.1-50$ Hz is superimposed to a static force F_{stat} , yielding both, real and imaginary parts of the complex elastic compliance $S^*=S'+iS''$ by measuring the corresponding dynamic amplitude u and phase angle δ , i.e.

$$\frac{u}{F} = \frac{S(\mathbf{q})}{4t} \left(\frac{L}{h} \right)^3 \left(1 + \frac{3h^2}{2L^2} \cdot \frac{S(\mathbf{p}, \mathbf{q})}{S(\mathbf{q})} \right) e^{i\delta} \quad (1)$$

where L , h and t are the length, span and thickness of the sample bar, respectively. \mathbf{q} points along the long axes of the sample bar and \mathbf{p} is the direction of the applied force F . $S(\mathbf{q})$ and $S(\mathbf{p}, \mathbf{q})$ are the longitudinal and shear components of the elastic compliance tensor, respectively. The corresponding Young's modulus is defined as $Y := 1/S$. Since in most cases $\frac{h}{L} \approx 10^{-2}$, the second part in Eq.(1) can be usually neglected. However, approaching a proper ferroelastic transition, $S(\mathbf{p}, \mathbf{q}) \rightarrow \infty$ and the second term in Eq.(1) can easily overcome the first one, making three point bending an ideal method to measure ferroelastic softening, i.e. $Y(\mathbf{p}, \mathbf{q}) \rightarrow 0$ for $T \rightarrow T_c$.

Supposing a multidomain ferroelastic crystal is exposed to a stress $\sigma = \sigma_{stat} + \delta\sigma_{dyn}$ the width x_+ of energetically preferred domains increases, whereas the width x_- of oppressed domains shrinks. This motion of domain walls leads to a macroscopic deformation ε^{DW} given as

$$f(\sigma) = f_L + k\varepsilon_s^2(x_+ + x_-) + \frac{1}{x_+ + x_-} [E_w + b \cdot \exp(-x_+/w) + b \cdot \exp(-x_-/w)] + 2\varepsilon_s \frac{x_+}{x_+ + x_-} \quad (5)$$

where $E_w > 0$ is the domain wall energy and $b > 0$ describes the repulsion of domain walls of finite width w and A , B , C are temperature independent Landau coefficients. The equilibrium conditions $\frac{\partial f(\sigma)}{\partial x_{\pm}} = 0$ lead to two transcendental equations which can be used [15] to calculate $x_+(\sigma, T)$ and $x_-(\sigma, T)$ and finally also $\Delta S^{DW}(\sigma, T)$. Here we focus on the elastic anomalies at very small applied stresses, i.e. for $\sigma \rightarrow 0$, yielding $x_+(0, T) = x_-(0, T) = d(T)$ and

$$\Delta S^{DW} = \frac{\varepsilon_s^2 w^2}{2bd} \cdot \exp(2d/w) \quad (6)$$

Eq.(6) is an extension of the classical results [21], where zero thickness of domain walls was assumed leading to a domain wall contribution to the corresponding elastic compliance $\Delta S^{DW} \propto \varepsilon_s^2/d$. The exponential term in Eq.(6) does not significantly contribute to the elastic anomaly since it is weakly temperature dependent, approaching unity at T_c . Thus we will omit this term for further considerations. Most importantly, in the present model $\Delta S^{DW}(T)$ is modified by the domain wall width squared $w^2(T)$. The temperature dependence of the domain wall width was measured [22] e.g. for LaAlO_3 yielding a temperature dependence of $w \propto (T_c - T)^{-1}$. For a Landau-Ginzburg Free energy expansion up to sixth or-

[15]

$$\varepsilon^{DW} = \varepsilon_s \left(1 - \frac{x_-}{2d} \right) \quad (2)$$

where ε_s is the spontaneous strain and d the average width of domains. Using Eq.(2), one obtains for the domain wall contribution to the elastic compliance

$$\Delta S^{DW} = \frac{\partial \varepsilon^{DW}}{\partial \sigma} = -\frac{\varepsilon_s}{2d} \left(\frac{\partial x_-}{\partial \sigma} \right) \quad (3)$$

Taking into account the long range elastic interactions between needle shaped domains and adding the repulsion between domain walls of finite thickness w to the Landau free energy density f_L

$$f_L = A(T - T_c)\eta^2 + B\eta^4 + C\eta^6 \quad (4)$$

one obtains the free energy density in the presence of applied stress as [15]

der and a one component order parameter η it was shown [23] that

$$w^2 = \frac{2g}{B\eta^2 + 2C\eta^3} \quad (7)$$

where g is the coefficient of the order parameter gradient term. The temperature dependence of the spontaneous strain in Eq.(6) depends crucially on the nature of the phase transition, i.e. on the coupling between the order parameter η and the strain variables ε , i.e. $\varepsilon_s \propto \eta^2(T)$ for *improper* and $\varepsilon_s \propto \eta(T)$ for *pseudo proper* ferroelastic phase transitions [6]. For *proper* ferroelastic phase transitions the order parameter is identical with the spontaneous strain, i.e. $\varepsilon_s \propto (T_c - T)^{1/2}$ for a 2-4 Landau free energy expansion.

Now we can use Eq.(6) and Eq.(7) to calculate the domain wall contributions to the elastic compliance. For *improper* ferroelastic materials one obtains:

$$\Delta S^{DW} \propto \frac{N_w \eta^2}{B + 2C\eta} \quad (8)$$

where $N_w \propto 1/d$ is the number of domain walls in the sample.

For *proper* ferroelastics we can write:

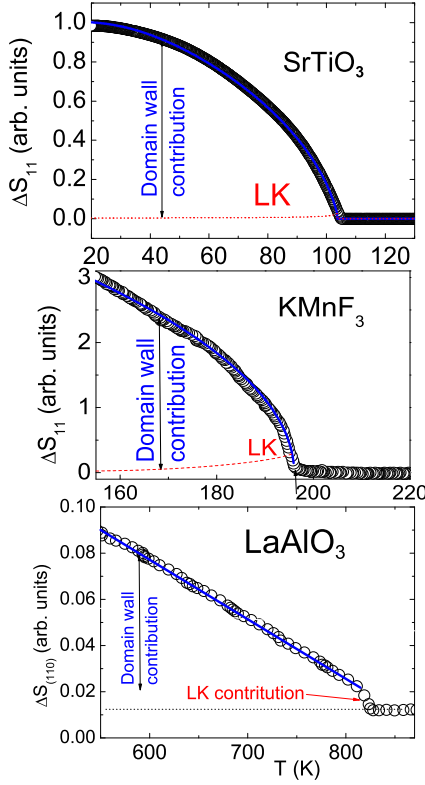


FIG. 1. DMA data of the anomalous parts of the elastic compliances of SrTiO_3 , KMnF_3 and LaAlO_3 (points) and corresponding fits (blue lines) using Eq.(8). LK is the elastic anomaly calculated for a monodomain crystal, taking into account the order parameter strain coupling in the corresponding Landau free energy.

$$\Delta S^{DW} \propto \frac{N_w}{B + 2C\varepsilon_s} \quad (9)$$

and for the *pseudo proper* ones we get:

$$\Delta S^{DW} \propto \frac{N_w}{B + 2C\eta} \quad (10)$$

Equations (8)-(10) imply that the domain wall contributions to the elastic compliance are very different for the various cases. For *improper* ferroelastics the anomaly in ΔS^{DW} is mainly determined by the temperature dependence of the number of domain walls $N_w(T)$ and the order parameter squared $\eta^2(T)$, whereas for *pseudo proper* and *proper* ferroelastics it is dominated by $N_w(T)$ only. In the following we will demonstrate, that these equations describe the experimental data of many rather different ferroelastic materials very well. Fig.1 shows the temperature dependencies of the compliances of three perovskites measured by DMA [8, 9, 24]. Both, SrTiO_3 and KMnF_3 undergo a cubic-tetragonal phase transition of

second [25] and weakly first order [26], respectively, described by a Landau free energy expansion up to sixth order (2-4-6 Landau potential), i.e. $B, C \neq 0$ in Eq.(4). LaAlO_3 undergoes a second order phase transition from rhombohedral to monoclinic structure, described by 2-4 Landau potential, i.e. with $C = 0$. In all these cases the behaviour of ΔS^{DW} is governed by the temperature dependence of the order parameter only, since the number of domains was found to be constant in the whole measured temperature range. Note that the temperature dependencies of the order parameters in SrTiO_3 [25], KMnF_3 [26] and LaAlO_3 [24] were determined very detailed, so there is not much freedom for fitting these data. Nevertheless, as Fig.1 shows Eq.(8) yields excellent fits for all three cases. A very similar behaviour has also been found for $\text{Pb}_3(\text{PO}_4)_2$ [27]. It exhibits a first order rhombohedral-monoclinic phase transition, described by a 2-4-6 Landau potential, leading to a nonlinear Domain wall contribution to the elastic compliance similar as for the other 2-4-6 perovskites. The most important result for this part is, that for all these *improper* ferroelastic cases $\Delta S^{DW} \rightarrow 0$ as $T \rightarrow T_c$.

Now we will focus on the pseudo proper or proper ferroelastic cases. $\text{La}_{1-x}\text{Nd}_x\text{P}_5\text{O}_{14}$ (LNPP) [28] as well as $\text{NdP}_5\text{O}_{14}$ (NPP) [17] undergo a second order proper ferroelastic phase transition at $T_c \approx 414$ K from orthorhombic $Pn\bar{c}m$ to monoclinic $P2_1/c$. A fourth order expansion of the Landau potential in terms of the shear strain ε_5 as primary order parameter describes the phase transition very well [17, 28]. Below T_c the crystal splits into ferroelastic domains forming a regular stripe pattern with opposite shear strain $\pm\varepsilon_5$. The number of domains increases from about 20/mm to about 180/mm for LNPP and even more drastically from about 100/mm to 1500/mm for NPP when approaching T_c from below. The transverse elastic constant C_{55} has been measured in LNPP by a resonator method at several tens kHz [28]. Fig.2 displays the shear compliance $S_{55} = C_{55}^{-1}$, which should exhibit a Curie-Weiss temperature dependence (red dotted line), i.e. $S_{55} \propto |T_c - T|^{-1}$ in the single domain state. In contrast the experimental data (filled points) show significant domain wall contributions below T_c , which excellently scale with the measured number of domain walls, as predicted from Eq.(9).

Finally we show the results for $\text{NH}_4\text{HC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$. Ammonium hydrogen oxalate hemihydrate (AHO) exhibits a pseudo proper ferroelastic phase transition of second order at $T_c = 146$ K [29] from $Pm\bar{n}b$ to $P2_1/n$. The bilinear coupling between the primary order parameter η and the shear strain ε_5 leads to a softening of the shear elastic constant C_{55} which indeed was previously measured by Brillouin scattering [30]. The corresponding inverse shear elastic constant $S_{55} = 1/C_{55}$ of a single domain crystal is expected to follow a Curie-Weiss type law [30] given as

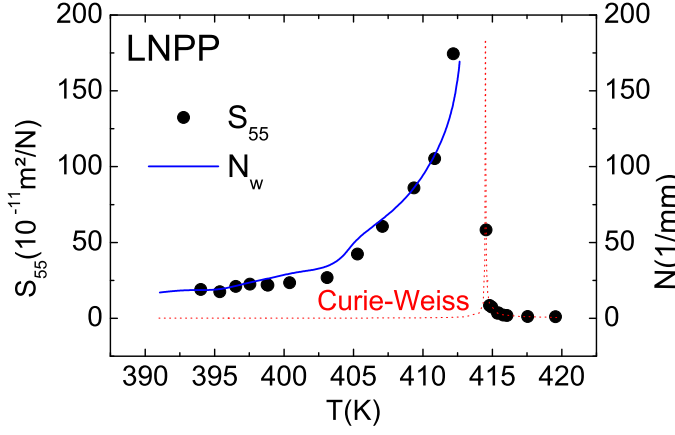


FIG. 2. Temperature dependence of the shear elastic compliance S_{55} (black points) of LNPP (from Ref.[28]) fitted with Eq.(9) using the experimental data of $N_w(T)$ (blue line). The red dotted line displays the Curie-Weiss law expected for a single domain crystal.

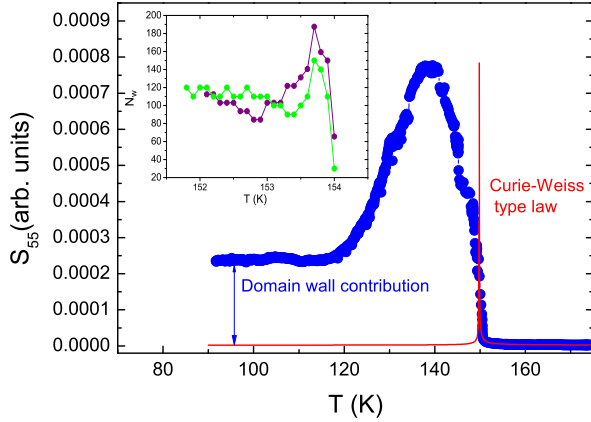


FIG. 3. Temperature dependence of the shear elastic compliance S_{55} of AHO measured with DMA7 in Three Point Bending geometry (blue points). The red line shows the Curie-Weiss type law Eq.(11) of a nomodomain crystal. The inset shows the temperature dependence of the number of domain walls N_w as determined from optical polarizing microscope measurements of two different AHO samples.

$$\begin{aligned} S_{55}^+ &= S_{55}^0 + \frac{T_c - T_0}{T - T_c} & T > T_c \\ S_{55}^- &= S_{55}^0 + \frac{T_c - T_0}{2(T_c - T)} & T < T_c \end{aligned} \quad (11)$$

where $T_c - T_0 > 0$, due to the bilinear coupling between η and ε_5 .

Fig.3 shows the temperature dependence of S_{55} of AHO measured by DMA in Three Point Bending Geometry at $f=1\text{Hz}$, which is in sharp contrast with the expected single domain behaviour.

The measured DMA data are described by Eq.(11) only *above* T_c . In the ferroelastic phase the measured data exceed the Curie-Weiss type anomaly by several orders of magnitude similar as for LNPP (Fig.2). The difference is due to domain wall motion. According to Eq.(10) the anomaly of S_{55}^{DW} is dominated by the temperature dependence of N_w which increases with $T \rightarrow T_c$ (see insert of Fig.3) in excellent agreement with the measured compliance data.

In conclusion we have shown, that for calculation of the macroscopic elastic response of multidomain crystals the finite width of domain walls and its temperature dependence has to be taken into account. In doing so, we have obtained excellent agreement with experimental data for quite a number of *improper*, *proper* and *pseudo proper* ferroelastic materials. It is expected, that these effects of domain wall thickness may be of similar importance also for other ferroic and multiferroic materials including also shape memory materials [31].

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